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Electrocatalytic Conversion of Small Molecules Utilizing Concerted Proton-electron Transfer Mediators

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Abstract: Activation of small molecules such as CO_2, N_2 or organic substrates and their subsequent transformation into complex value-added chemicals by electrocatalysis, utilizing renewable energy sources under ambient conditions, has gained considerable interest in the last few years. However, activation of these chemically inert molecules is hindered by their intrinsically high activation energy barrier presupposing the development of tailored catalytic systems, often precluding selective transformation to the desired target products. Recent studies have shown that the utilization of concerted proton-electron transfer (CPET) mediators (med-H) may facilitate these challenging electrocatalytic reactions.

Keywords: CPET · Electrocatalysis · Mediator · Proton-coupled electron transfer

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1. Introduction

Proton-coupled electron transfer (PCET) reactions are present in a wide variety of chemical transformations, including energy-conversion and transfer of energy in biological systems[1] as well as in many artificial biomimetic systems.[2] Intricate PCET reactions play a key role in vital biochemical processes in nature, for example in the transformation of dinitrogen (N_2) to ammonia (NH_3) in the FeMo cofactor of the nitrogenase enzyme[3] and in the oxidation of formate ($HCOO^-$) to carbon dioxide (CO_2) by formate dehydrogenases.[4] Recently, such unique PCET processes have been utilized in the electrocatalytic reduction of N_2,[5,6] CO_2[7] and small organic molecules,[8,9] which typically require the coupling of the electron transfer step to a subsequent or preceding proton transfer step in several PCET reactions. In these catalytic reactions, concerted proton-electron transfer (CPET) mediators (med-H) act as key reagents to promote the transfer of one or mutliple hydrogen atom ($H^\bullet$ = $1e^-/1H^+$) equivalents, facilitating the electrochemical conversion of the target substrates.

The electrochemical transformation and utilization of CO_2 and N_2 by molecular transition metal catalysts has been widely studied in the last few decades (Fig. 1b).[3,10,11]

Carbon monoxide (CO) and formic acid (HCOOH) are some of the desired target products in the electrochemical CO_2 reduction reaction (CO_2RR), requiring the transfer of $2e^-$ and $2H^+$ respectively.[10][12] Selectivity towards the desired product can be achieved by unlocking different mechanistic pathways through kinetic differentiation.[10,13] Formation of CO has been commonly observed in electrocatalytic CO_2RR with group VII transition metals complexes,[10] specifically manganese (Mn)[14] and rhenium (Re)[15] bearing multidentate redox non-innocent bipyrdine derived ligands as well as for many group VIII transition metal complexes of iron (Fe)[10] and ruthenium (Ru).[10] Studies on the selective electrochemical reduction of CO_2 to HCOOH/$HCOO^-$ evidenced the occurrence of transient metal hydride (M-H) species, acting as key reactive intermediates in the catalytic pathway.[10,16]

In contrast, the chemical fixation of N_2 by transition metal complexes[17–19] and its subsequent catalytic transformation un-

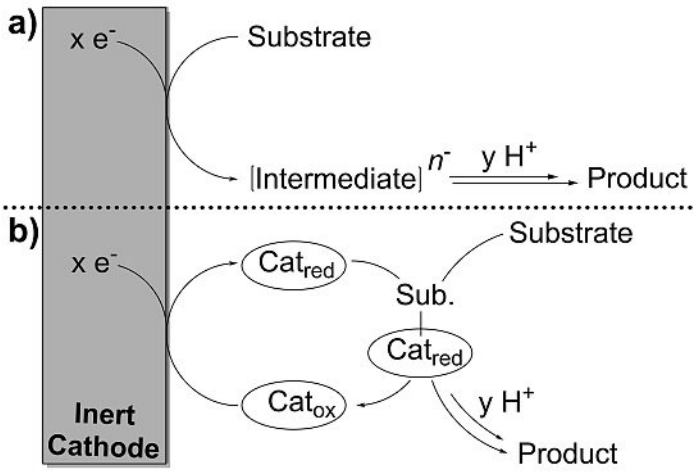

Fig. 1. General scheme depicting a) the direct electrochemical reduction and b) the transition metal catalyzed electrochemical reduction of a substrate.

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der ambient conditions remains a challenging task.[11] The N≡N triple bond has a considerable thermodynamic strength (bond dissociation enthalpy of 944 kJmol^{-1}).[11] Furthermore, N_2 has a high kinetic inertness towards reduction, partially due to the fact that it is a non-polar molecule, lacking a permanent dipole moment.[3,11] Moreover, to date only a limited number of studies on the electrocatalytic conversion of N_2 to NH_3 have been published.[5,19,20]

In this perspective, the basic framework of PCET reactions will be briefly discussed, followed by an overview of selected examples on the emerging use of CPET med-H in homogeneous electrocatalysis. For more extensive discussion on PCET reactions[21–23] and studies on PCET reactivity on heterogeneous surfaces[24–26] please refer to the cited literature.

1.1 *Defining PCET Reactivity and Reactions*

Fundamentally, a PCET is a reaction involving the transfer of one or multiple electrons and protons (xe^-/yH^+),[27] whereas in the current text the discussion will be limited to the transfer of an equal number of electrons and protons. PCET processes inherently involve energetic coupling between electron transfer (ET) and proton transfer (PT).[28] This is exemplified by the observation that for a sequential ET-PT pathway (or *vice versa* PT-ET), the reduction potential ($E_{red}°$) is shifted based upon prior (de)protonation steps, described as the difference in the reduction potential $\Delta E_{red}°$. The resulting correlation of $\Delta E_{red}°$ related to the difference in pK_a is described by $\Delta E_{red}° = 0.059 \cdot \Delta pK_a$ and can be deduced from the Nernst-equation for a $1e^-/1H^+$ process.[28] Large values for $\Delta E°$ and ΔpK_a qualitatively translate into a strong energetic coupling of the sequential ET-PT/PT-ET steps respectively, which has been shown systematically on a biomimetic series of tyrosine derivatives mimicking artificial photosynthetic relays.[29] The coupling of electron and proton transfer does not only influence the thermodynamics of a reaction but also its inherent kinetics, resulting in differentiating mechanistic pathways.[27,28,30] The rigorous mathematical description of the kinetics of PCET processes has been described in detail in the referenced reviews by Hammes-Schiffer and coworkers[31,32] and will not be further developed here.

The sequential transfer of electrons and protons respectively (ET-PT/PT-ET), hydride transfer (simultaneous transfer of $2e^-/1H^+$) and concerted proton-electron transfer (CPET, transfer of $1e^-/1H^+$ in a single kinetic step) are all possible elementary steps by which a PCET reaction may occur.[27] CPET reactions have been commonly divided into H-atom transfer (HAT, transfer of $1e^-/1H^+$ from the same chemical bond) and multiple-site CPET (MS-CPET) involving the concerted transfer of e^- and H^+ from different donors or donor sites to a common acceptor or *vice versa*.[27]

Focusing on a sub-section of available PCET reactions, the concerted proton-electron transfer (CPET) is of specific interest in electrocatalytic applications. In a CPET-pathway, the proton/s and electron/s are transferred in a single kinetic step (H$^•$-atom equivalent/s), traversing a common transition state with only one associated activation barrier as depicted in the thermochemical square scheme, Fig. 2.[28,30] In this context, the term hydrogen-atom equivalent/s (H$^•$-atom equivalent/s) will be used to refer to any reaction where one or multiple electron/s and proton/s are transferred in a concerted pathway. Consequently, this type of concerted reactivity bears a kinetic advantage to the sequential pathways. The promotion of a CPET process presupposes strong energetic coupling between the ET-PT step respectively and requires a CPET med-H which is able to transfer a hydrogen atom equivalent in a single kinetic step, to either a substrate or a metal center, and which may be subsequently regenerated by accepting an electron from an inert electrode and a proton from the electrolyte.[7] Generally, the applied electrochemical bias required for a catalytic reaction can be considerably lowered when the initial or rate determining step is a CPET.[2]

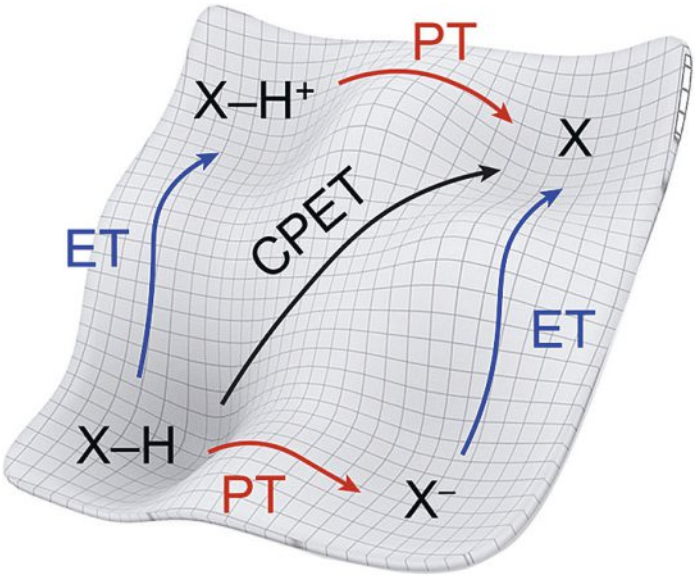

Fig. 2. Free energy surface of a PCET reagent (X-H), depicting the CPET pathway on the diagonal and the sequential ET-PT/PT-ET pathways respectively. Reprinted with permission from *Chem Rev* **2022**, *122*, 1.[30] Copyright 2022 American Chemical Society.

In a sequence of multiple redox-reactions, coupled with multiple (de)protonation steps, the buildup of charged intermediates may significantly heighten the associated energy barrier of a reaction due to a difference in reorganization energy.[28] In comparison, the overall transfer of an apparent hydrogen atom equivalent ($1e^-/1H^+$) is a charge neutral reaction and therefore energetically advantageous in non-polar solvent mixtures and in hydrophobic environments of proteins.[2,28] It is evident from the prior discussion, that the experimental differentiation between a sequential PCET and a CPET mechanism may often be challenging. In 2018, a thorough mechanistic study on the identification of switching pathways between stepwise PCET and CPET in the activation of a series of tungsten hydride complexes has been published.[33] All limiting pathways of PCET (sequential PT-ET/ET-PT and CPET) were accessible as a function of the intrinsic electronic properties of the studied transition metal complexes and by variation of the experimental activation conditions.[33]

1.2 *Thermochemistry of PCET Reagents*

A key thermochemical parameter to describe PCET reagents is the solution bond dissociation free energy ($BDFE_{solv}$) of a chemical bond.[30] The $BDFE_{solv}$ is formally specified as the homolytic cleavage of an X-H (X = heteroatom) bond into its components to give X$^•$ and H$^•$ (Equation 1).

$$XH \rightarrow X^• + H^• \qquad \Delta G° = BDFE \tag{1}$$

As a result, the $BDFE_{solv}$ of a species can be derived from rigorous thermochemical component calculations. The $BDFE_{solv}$ of an X-H bond is the combination of a bond dissociation enthalpy (BDE) term and an additional entropy contribution of the individual components (XH, X$^•$ and H$^•$) in the respective solvent.[30] However, the entropy terms of HX and X$^•$ are generally not easily accessible experimentally, whereas the thermochemistry of H$^•$ solvation in numerous solvents has been well established in literature.[30] In order to convert BDE_{solv} to $BDFE_{solv}$, the common assumption is made that the absolute entropies of X$^•$ and XH are dominated by the contribution of the heteroatom X due to similarity in atom-size and polarity, there-

fore cancelling each other and simplifying the final expression to (Equation 2).[30]

$$\mathrm{BDFE(XH)_{solv} = BDE(XH)_{solv} - }T\mathrm{S^{\circ}(H^{\cdot})} \qquad (2)$$

Multiple formalisms have been developed relating the $BDFE_{solv}$ values of PCET reagents to a relevant parameter set accessible in an electrochemical experiment.[30,34] Bordwell originally developed such an approach by partitioning the $BDFE_{solv}$ into a free energy contribution for the electron transfer and a free energy contribution for the proton transfer, which can be described in an empirical formula as a function of a one e^- reduction potential, the pK_a value of the protonated species and a solvent-dependent constant C_G (Equation 3).[34]

$$\mathrm{BDFE} = 23.06E^{\circ} + 1.37\mathrm{p}K_a + \mathrm{C_G} \qquad (3)$$

This equation can be used to determine $BDFE_{solv}$ for reagents which react according to a PCET mechanism either in a concerted or a non-concerted fashion. C_G is a composite value and is defined as the contribution of a constant for homolytic H_2 dissociation to $H^{\cdot}$ in the gas phase, summed with the free energy contribution of $H^{\cdot}$ solvation in the respective solvent of interest.[30] Both free energy contributions are related with respect to the potential of hydrogenation $E^{\circ}(H^+/H_2)$ determined in the specific solvent of interest as a fundamental reference state.[30] Comprehensive studies exist on tabulated BDFE values of PCET reagents relevant for electrocatalytic applications.[30,35] Related to this, Mayer and coworkers have recently reported a novel series of ruthenium based $Ru^{II}(acac)_2(py\text{-}imH)$ (acac = acetylacetonate, py-imH = pyridine-imidazole) complexes in which the redox and (de)protonation properties were tuned independently of each other by tailoring the substitution pattern on the ligand scaffolds.[36] Across a series of structurally similar compounds, merely small variations in $BDFEs_{solv}$ are generally observed, which is caused by the thermodynamic compensation (coupling) between the redox potential and the pK_a of a species.[30,36] Decoupling of the two parameters resulted in a wide range of obtainable BDFE values for the relevant N-H bond on the imidazolyl moiety.[36] Analogous decoupling has also been observed in another study on cobaltocenium based complexes which have been utilized as CPET med-H.[5,6,8]

In recent years, a number of novel approaches for the description of PCET reagents have been developed, introducing the potential of hydrogenation E°(V *vs* H_2) as a thermochemical parameter in non-aqueous systems, which is referenced to the reversible hydrogen potential (RHE, H^+/H_2) and can be easily related to $BDFE_{solv}$ values.[30] Concurrently, the experimental determination of the RHE potential in non-aqueous systems has been made readily accessible by open-circuit potential measurement protocols developed by Roberts and Bullock.[37]

2. Electrocatalytic Utilization of CPET Mediators

We will introduce here a selection of applications of CPET mediators in homogeneous electrocatalysis. In the following discussion we will differentiate between PCET to a substrate (either coordinated (Fig. 3a) or non-coordinated by a metal center) and PCET to a reduced metal center (Fig. 3b), generating a reactive metal hydride (M-H) species. We concede the simplification we postulate here, taking into account that PCET reactions to a substrate in transition metal electrocatalysis may possibly also involve the generation of transient M-H species which are merely too short-lived to be observed during the catalytic reaction. In the case of the latter pathway, the formed M-H acts as the catalytically active species by promoting the downstream reduction of a target substrate. In close analogy, the reverse reaction, namely the electrochemical oxidation of transition M-Hs, promoted by regenerable hydrogen atom acceptor mediators has been pioneered by Waymouth and coworkers for the electrocatalytic alcohol oxidation reaction[38] which will not be further discussed in the following paragraphs.

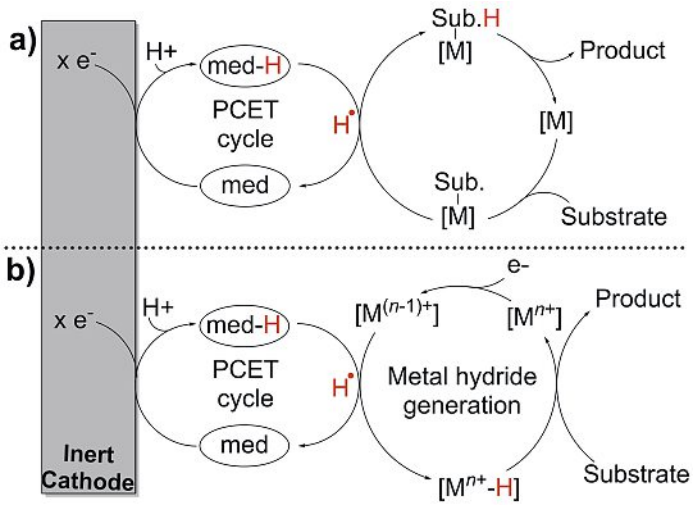

Fig. 3. Electrocatalytic PCET to a) a substrate and PCET to b) a reduced transition metal center to form a M-H species. Both pathways are promoted by a CPET med-H species.

2.1 *PCET to a Substrate*

In 2022, Peters and coworkers reported the first example of electrocatalytic N_2 reduction by a tandem approach, utilizing the tungsten based *trans*-$(dppe)_2W(N_2)_2$ dinitrogen fixation catalyst previously reported by Pickett[20] in combination with a cobaltocenium based CPET med-H in the presence of a proton source.[5] Under optimized conditions an impressive faradaic efficiency of 43% towards ammonia was obtained. Most strikingly, use of the cobaltocenium based CPET mediator, modified with a tethered aniline-derived Brønsted base, lowered the required overpotential for electrocatalytic N_2 reduction with *trans*-$(dppe)_2W(N_2)_2$ by 1.25 V compared to Pickett's original report,[20] considerably increasing the catalytic activity.[5,20] These findings evidence, that the applied electrochemical bias required for catalysis may be substantially lowered by a CPET pathway. Key to this enhanced reactivity is the transfer of multiple $H^{\cdot}$-atom equivalents from the mediator to the coordinated N_2 moiety[5] (Fig. 3a), likely by a distal associative pathway. The molecular architecture of the mediator enables the structural separation of the electron transfer relay from the site of protonation on the molecule, in turn reducing competing hydrogen evolution reaction (HER) during catalysis.[5] In a prior study utilizing a similar cobaltocenium based mediator, the electrocatalytic conversion of small organic molecules by the transfer of one $H^{\cdot}$-atom equivalent per molecule of substrate in a concerted pathway was reported.[8] This unique reactivity was correlated to the redox-induced bond weakening[39,40] of the relevant N-H bond in the protonated mediator upon the reduction of Co^{III} to Co^{II}, considerably lowering the effective $BDFE_{solv}$ of the species.[8]

2.2 *PCET to a Metal Center*

The generation of transient M-H species during reductive electrocatalysis in presence of abundant protons often leads to dominating HER as a competing side-reaction.[7,9] A key approach to suppress the HER in electrocatalysis is the generation of the catalytically active species at potentials anodic of the onset potential of H_2 formation. This can be facilitated by the transfer of a $H^{\cdot}$-atom equivalent from a CPET med-H to a reduced metal center to form a reactive M-H species (Fig. 3b).[7,9]

As a proof of concept, our group investigated the known electrocatalyst [Mn^{I}(bpy)$(CO)_3$Br] (Mn^{I}-cat) in combination with a series of CPET mediators for the electrocatalytic CO_2RR.[7] A novel strategy was developed where a biomimetic iron-sulfur cluster $[Fe_4S_4(SPh)_4]^{2-}$ (FeS) was utilized as an H•-atom equivalent transfer mediator for the electrocatalytic generation of a Mn^{I}-H species by a CPET mechanism (Fig. 4).[7] Notably, the generation of the active species involves the transfer of a H•-atom equivalent (e^-, H^+) from the reduced CPET med-H to the singly reduced metal center [$M^{(n-1)+}$] to generate the Mn^{I}-H species.[7] The formed Mn^{I}-H acts as the major catalytically active species, promoting the selective reduction of CO_2 to HCOOH.[7] Consequently, a complete reversal in the selectivity of the formed product from CO to HCOOH was observed in a faradaic efficiency of 92%, while maintaining low levels of H_2 formation by circumventing the competing HER.[7]

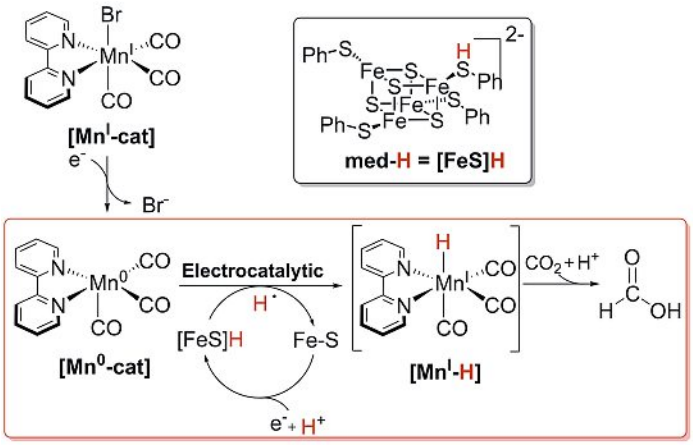

Fig. 4. Reaction pathway for Mn^{I} promoted electrocatalytic CO_2RR, facilitated by a biomimetic iron-sulfur (FeS) cluster as med-H.[7]

The proposed mechanistic pathway agrees well with previous studies in the field of electrocatalytic CO_2RR, evidencing that the occurrence of transient M-H species governs the selectivity of CO *vs* $HCOO^-$/HCOOH formation.[10,39] Thermodynamic boundary conditions for CPET mediated M-H formation were postulated on the basis of BDFE and pK_a values (Eqations 4 and 5).[7] For a CPET reaction to take place from the med-H to the one e^- reduced manganese center, the BDFE of the med-H ($BDFE^{med\text{-}H}$) has to be lower than the BDFE of the formed Mn^{I}-H species ($BDFE^{M\text{-}H}$).[7] Secondly, to efficiently regenerate the CPET mediator, the pK_a of the proton source ($pK_a^{H+\text{-donor}}$) has to be lower than the p*K*a of the med-H ($pK_a^{med\text{-}H}$).[7]

$$BDFE^{M\text{-}H} > BDFE^{med\text{-}H} \quad (4)$$

$$pKa^{H^+\text{-donor}} < pKa^{med\text{-}H} \quad (5)$$

Moreover, a recent study by Peters and coworkers described the electrocatalytic generation of a Ni^{II}-H species promoted by a cobaltocenium derived CPET med-H.[9] The formed Ni^{II}-H species was found to be active in promoting the catalytic semi hydrogenation of organic model substrates such as α,β-unsaturated ketones by means of hydride transfer under mild conditions.[9] Based on the spectroscopic and electrochemical investigation of the catalytic system a rate-determining PCET step was identified, which is key to generate the active Ni^{II}-H.[9]

Current research in our group focuses on the study of the CPET mediation properties for a series of biomimetic iron-sulfur clusters, investigating the variation of their respective BDFE values for catalysis and other applications.

3. Conclusion

The application of CPET med-H in homogeneous electrocatalysis has proven effective to enable challenging electrochemical transformations under ambient conditions. This has been exemplified on the example of the electrochemical transformation of inert, small molecules such as CO_2 and N_2. Furthermore, CPET med-Hs have been successfully employed as promoters in the field of organic electrosynthesis, providing an atom-economic alternative for the chemical industry. While providing an overview on the valorization of chemically vastly different substrates, this perspective emphasizes that the investigation of catalytic pathways, identification of key reactive intermediates and experimental conditions is crucial to understand reactivity and resulting product selectivity in PCET mediated electrocatalysis.

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